

(Addison-Wesley, Reading, MA, 1955), p. 3.

<sup>3</sup>J. R. Reitz, F. J. Milford, and R. W. Christy, *Foundations of Electromagnetic Theory*, 3rd ed. (Addison-Wesley, Reading, MA, 1979), p. 44.

<sup>4</sup>M. J. Lighthill, *Fourier Analysis and Generalized Functions*, students' ed. (Cambridge University, Cambridge, England, 1964), pp. 18–24.

<sup>5</sup>J. D. Jackson, Ref. 1, p. 141.

<sup>6</sup>R. H. Good and T. J. Nelson, *Classical Theory of Electric and Magnetic Fields* (Academic, New York, 1971), pp. 222–224.

<sup>7</sup>I. M. Gel'fand and G. E. Shilov, *Generalized Functions* (Academic, New York, 1964), Vol. I.

<sup>8</sup>L. Schwartz, *Theorie des Distributions* (Hermann, Paris, 1950), Vol. I.

<sup>9</sup>J. D. Jackson, Ref. 1, pp. 138 and 182.

## How batteries work: A gravitational analog

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There is a region in any battery where the charges move in a direction opposite to that of the electric force on them. A “gravitational cell” is used to show that this motion is a diffusion analogous to that against pressure gradients in osmotic pressure situations. The driving mechanism for the diffusion is the existence of lower lying states in one region compared to an adjacent region, and it is relaxation into these low lying states that is the source of energy for the circuit.

### I. INTRODUCTION

When a moving magnet induces an emf in a circuit, it is relatively easy to see that whatever moves the magnet is the source of energy, and that the induced electric fields push the charges around the circuit. In batteries, thermoelectric devices, and the like, the situation is more subtle. In all these cases, a charge separation is maintained between two points, thus creating electric fields that can then do work. It is clear that chemical reactions or a heat source of some kind supplies the energy in these cases, but how these create a charge separation is more difficult to see. In fact, in any circuit with a maintained charge separation as the source of electric fields, there must be at least one region in which current carriers go in a direction *opposite* to the electric forces from the separated charges. There is no obvious force available to counterbalance the electrical force, so the question becomes how batteries work at all. Many authors and teachers have been tempted to introduce “chemical electric forces” to do the trick. The main point of this article is that no such fictions are needed. Of course a particle moving against an opposing force will slow down, but this may not matter. Even if the particle motions in one region are random, if there are lower energy (and thus more likely to be occupied) states available in a second, neighboring region, particles will tend to accumulate in the second region even if they have to overcome a potential barrier to do so. These ideas are spelled out in the following argument.

### II. THE PROBLEM

A seat of emf is a device that maintains electric fields. The maintained field can do work, thus making the seat a useful device. Electric fields can be created only by changing magnetic fields or by charge separation. The cases of interest in this paper involve at most steady-state magnetic fields, and thus they must rely on charge separation. More-

over, for these situations, Faraday's law states

$$\oint \mathbf{E} \cdot d\mathbf{l} = 0, \quad (1)$$

since there is no changing magnetic flux. This implies that there must be regions in which the dc charge flow, which goes in one direction around the circuit, must be *opposite* to the electric force on it, since this is the only way to get cancelling contributions to the integral. In regions such as resistors, charges flow in the direction of electric forces, and energy is transferred to charges. In the regions where the electric force opposes charge flow, energy is added to the fields at the expense of particle energy; this must be the case in the seat of emf, since the seat is the source of energy for the circuit, by definition. More formally, letting  $\mathbf{J}$  be the current density in the circuit,  $\mathbf{E} \cdot \mathbf{J}$  must be negative in the

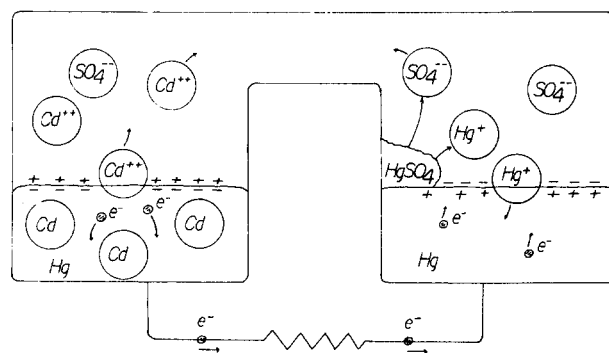


Fig. 1. Weston cell in operation. Note the double layers, across which  $\text{Cd}^{++}$  and  $\text{Hg}^{+}$  ions pass *against* electric forces, while ions and electrons flow *with* the electric forces in the electrolyte and the resistor, respectively. It is the fact that electrons have lower energy states available to them on Hg atoms than on Cd atoms that makes the cell a source of electrical energy. (After E. M. Purcell, Ref. 1.)

seat of emf, leading to an increase in field energy. (Of course, in the steady state the sources and sinks of field energy operate at the same time, thus maintaining a constant field energy.)

The puzzle of batteries and the like is to see how it is that charges manage to move against the electrical forces on them. In the case of a Van de Graff generator, the charges are simply mechanically pushed against the field in order to maintain the charge on the collecting surface.<sup>1</sup> The problem comes in seeing, for example, how chemical reactions can produce the same counterintuitive charge motion. The natural tendency of most people is to say the answer is that some microscopic "chemical electric field" is at work pushing the charges, but if this were the case there would be no  $\mathbf{E} \cdot \mathbf{J} < 0$  region, and no seat of emf. After a description of the usual situation in a battery is presented, this dilemma will be resolved by the use of a gravitational analogy.

### III. TYPICAL CHEMICAL CELL

Figure 1 shows the details of a Weston cell, which is typical of chemical cells.<sup>2</sup> The left-hand mercury electrode has cadmium dissolved in it, and some  $\text{HgSO}_4$  provides ions for the electrolytic solution on the right. The dissolved Cd tends to go into solution as  $\text{Cd}^{++}$ , leaving behind two electrons per atom, thus making the left-hand electrode negative. The right-hand electrode becomes positive as mercury ions join the neutral Hg atoms. The resulting "double layer" charge distributions on the surfaces of the electrodes make electrons flow in the external circuit, and ions flow in the electrolyte. Only the ionic motion across the double layer is opposed by electrical forces.

The width of the double layer can be roughly understood as the result of forces of electrical attraction working to hold together oppositely charged particles that are trying to fly apart due to their thermal motion. It is a difficult, nonlinear problem to find the actual charge distribution in such a layer,<sup>3</sup> but it is clear that either a higher temperature or a lower charge density will tend to increase the width of the layer. In a plasma this balance is expressed through the "Debye length,"  $\lambda_D$ , given in terms of the temperature  $T$ , and charge density  $n$ , by<sup>4</sup>

$$\lambda_D = (kT/4\pi e^2 n)^{1/2}, \quad (2)$$

where  $k$  is Boltzmann's constant and  $e$  is the electronic charge. For  $T = 300$  K and  $n = 10^{18} \text{ cm}^{-3}$ , the Debye length is  $10 \text{ \AA}$ , which is about the right value for the width of a double layer. This implies that the true seat of emf is in a very small region in which a "contact potential" is set up. This double layer region opposes charge motion with large electric fields (about  $1 \text{ V}/1 \text{ \AA} = 10^7 \text{ V/cm}$ ) over a very short distance. More generally, whenever two dissimilar materials are in contact, a contact potential is set up<sup>5</sup>; it is this that we must understand to see how batteries work.

### IV. CONTACT POTENTIALS IN A GRAVITATIONAL ELECTRODE

Contact potentials can be readily understood in a case where the source of energy is gravitational, rather than chemical. Suppose equal numbers of atoms at temperature  $T$  are placed on either side of a narrow box in which the left-hand side of the box has its bottom at  $z = 0$ , and the right-hand side at  $z = h_0$ . (See Fig. 2.) The two sides have equal width and depth into the page, and the top of both sides will

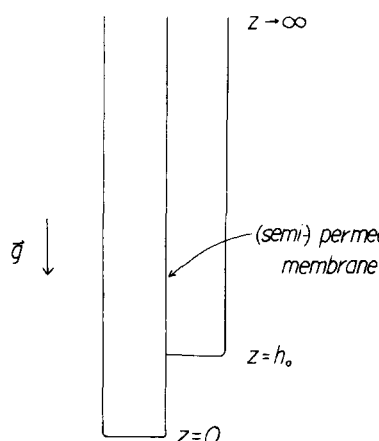


Fig. 2. Model "gravitational electrode."

be taken to be infinitely high. If the box is in a downward gravitational field  $g$ , then the number density of atoms will decay exponentially with height, but the density will be greater at a given height on the right-hand side of the box than on the left. If the partition becomes permeable to the atoms, the two sides will eventually have equal number densities of atoms at a given height, and thus the atoms will have become redistributed such that

$$N_l = N_r e^{mgh_0/kT}, \quad (3)$$

where  $m$  is the atomic mass,  $k$  is Boltzmann's constant, and  $N_l$  and  $N_r$  are the numbers of atoms on the left-hand and right-hand sides of the box. The existence of available lower energy states on the left-hand side of the box leads to a net diffusion of particles to the left. Note that no force was needed to push the particles to the left: they simply wandered over.

Suppose now that the original atoms on both sides are half plus charged and half minus charged, and that the partition is only permeable to the positive atoms. There will still be a diffusion across the partition, but it will be resisted to a progressively greater extent by the increase in potential across the partition set up by the increasing charge separation as the diffusion proceeds. The equilibrium set up will be characterized by a smaller number difference than that implied by Eq. (1), but with a potential difference across the partition that will give them the emf of this "gravitational electrode."

To make this idea more quantitative, we need to consider in greater detail the problem of diffusive equilibrium between two regions when gravitational and electric potentials are present. The energy balance between different regions in thermal equilibrium is determined by the equality of the temperatures in the regions. The quantity that similarly tells us about the particle number balance between the regions is the "chemical potential"; in thermal equilibrium the chemical potential is a constant in a system.<sup>6</sup> The chemical potential can be introduced by stating that it tells us how the free energy  $G$ , changes with number,  $N$ :

$$\mu = \frac{\partial G}{\partial N} \quad (4)$$

or statistically by the generalization of the Boltzmann factor appropriate for the grand partition function:

$$e^{-E/kT} \rightarrow e^{-E/kT + \mu N/kT}. \quad (5)$$

Evaluating the chemical potential from this starting point

gives, for an ideal gas,<sup>1</sup>

$$\mu = kT \ln(n/n_0) + U(\mathbf{r}), \quad (6)$$

where  $n_0$  is an arbitrary reference density and  $U(\mathbf{r})$  is the potential energy function, here given by

$$U(\mathbf{r}) = mgh + e\phi \quad (7)$$

with  $\phi$  being the electric potential as a function of position. Note that in the uncharged atom case, the equality of chemical potentials across the permeable membrane gives the equality of densities used to derive Eq. (3).

In the case at hand, if we consider connecting wires to the bottoms of the two sides of the charged-atom box, the equality of chemical potentials gives

$$kT \ln(n_l/n_0) + e\phi_l = kT \ln(n_r/n_0) + mgh_0 + e\phi_r \quad (8)$$

or

$$\mathcal{E} = \phi_l - \phi_r = mgh_0/e - (kT/e) \ln(n_l/n_r) \quad (9)$$

for the emf of the electrode. Here  $n_l$  and  $n_r$  are the number densities of particles at the bottom of the left-hand and right-hand side of the box. This expression is similar to that predicted for a chemical electrode,<sup>8</sup> and exhibits roughly the correct temperature dependence to explain thermocouple emf's.

In both the charged and the uncharged atom cases, there is a decrease in the gravitational potential energy of the atoms in the diffusion process, since the center of mass of the atoms moves down. In the uncharged atom case, if the diffusion occurred adiabatically, then there would be an increase in the temperature inside the box. In the charged atom case, the potential energy would go into both electric and thermal energy. If the processes occurred at constant temperature, a box with charged atoms would give off less heat than one with uncharged atoms. Note that even in the charged atom case, it is the thermal momentum of the positive particles that carries them across the boundary. In the process of moving against the potential gradient, the atoms lose kinetic energy. This means that less energy must be given off (compared to the uncharged case) to have these particles attain thermal equilibrium on the left-hand side of the box. No extra electric field or any other horizontal force is needed to understand this situation.

Since there is a density difference at constant tempera-

ture here, it is tempting to say that a pressure gradient drives the atoms across the boundary. The irrelevance of pressure equilibrium can be seen by noting that we could add appropriate numbers of neutral atoms—of a species for which the (rigid) membrane is impermeable—to both sides of the box to equilibrate the pressures at a given height before the diffusion occurs. When the positive atoms are then allowed to diffuse, the process will occur much as before, except that now there will be an osmotic pressure buildup. Thus an emf will still result, even though *both* pressure and electrical potential gradients oppose the particle motion.

In the thermocouple and chemical cell cases, the differences in available energy states are determined by quantum mechanics, and concentration gradients will be relevant in, for example, driving ions into solution. Nevertheless, the basic mechanism is the same: there is a net differential motion of charged species due to the existence of adjacent regions that have states that are unequally likely to be occupied. In each case, the emf comes about through a diffusion process in which charges move against electric forces, thereby losing kinetic energy to electric field energy. There is no problem at any stage of this process with either energy conservation or force laws, and there is no need to invoke chemical electric fields as some authors have done.

<sup>1</sup>This example is discussed in E. M. Purcell, *Electricity and Magnetism* (McGraw-Hill, New York, 1965), pp. 134–135. This and other interesting examples can be found in E. M. Pugh, *Am. J. Phys.* **29**, 484 (1961).

<sup>2</sup>This cell is described in Ref. 1, p. 136.

<sup>3</sup>A similar situation is that of a “plasma sheath,” discussed in F. F. Chen, *Introduction to Plasma Physics* (Plenum, New York, 1974), p. 244.

<sup>4</sup>Reference 3, p. 8.

<sup>5</sup>Noncontact charge separation emf's also exist, such as Thompson emf's, and the example discussed by R. P. Feynman, in *The Feynman Lectures on Physics* (Addison-Wesley, Reading, MA, 1964), Sec. 22-2. These emf's can also be explained using the techniques outlined in this paper.

<sup>6</sup>An excellent discussion of the chemical potential can be found in C. Kittel, *Thermal Physics* (Wiley, New York, 1969), Chap. 5.

<sup>7</sup>The calculation is carried out in Ref. 6, pp. 177–180.

<sup>8</sup>Various physical chemistry texts derive the chemical cell results. See, for example, K. Denbigh, *The Principles of Chemical Equilibrium*, 3rd ed. (Cambridge University, NY, 1971), p. 167.